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**UTILITY PATENT APPLICATION TRANSMITTAL**  
**(Large Entity)**

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Docket No.

10208-1

Total Pages in this Submission

40

**TO THE ASSISTANT COMMISSIONER FOR PATENTS**Box Patent Application  
Washington, D.C. 20231

Transmitted herewith for filing under 35 U.S.C. 111(a) and 37 C.F.R. 1.53(b) is a new utility patent application for an invention entitled:

**A CATALYTIC CRACKING PROCESS USING A MODIFIED MESOPOROUS ALUMINOPHOSPHATE MATERIAL**

and invented by:

Arthur W. Chester; Frederick E. Daugherty; Anthony S. Fung; Charles T. Kresge; HyeKyung C. Timken;  
James C. Vartuli; Ranjit Kumar; Terry G. Roberie; Michael S. Ziebarth

1C530 U.S. PTO  
09/468450  
12/21/99



If a **CONTINUATION APPLICATION**, check appropriate box and supply the requisite information:

Continuation    Divisional    Continuation-in-part (CIP) of prior application No.: \_\_\_\_\_

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Enclosed are:

**Application Elements**

1.  Filing fee as calculated and transmitted as described below
  
2.  Specification having 36 pages and including the following:
  - a.  Descriptive Title of the Invention
  - b.  Cross References to Related Applications (*if applicable*)
  - c.  Statement Regarding Federally-sponsored Research/Development (*if applicable*)
  - d.  Reference to Microfiche Appendix (*if applicable*)
  - e.  Background of the Invention
  - f.  Brief Summary of the Invention
  - g.  Brief Description of the Drawings (*if drawings filed*)
  - h.  Detailed Description
  - i.  Claim(s) as Classified Below
  - j.  Abstract of the Disclosure

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**Application Elements (Continued)**

3.  Drawing(s) (*when necessary as prescribed by 35 USC 113*)
  - a.  Formal Number of Sheets 1
  - b.  Informal Number of Sheets \_\_\_\_\_
4.  Oath or Declaration
  - a.  Newly executed (*original or copy*)  Unexecuted
  - b.  Copy from a prior application (37 CFR 1.63(d)) (*for continuation/divisional application only*)
  - c.  With Power of Attorney  Without Power of Attorney
  - d.  **DELETION OF INVENTOR(S)**  
Signed statement attached deleting inventor(s) named in the prior application,  
see 37 C.F.R. 1.63(d)(2) and 1.33(b).
5.  Incorporation By Reference (*usable if Box 4b is checked*)  
The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.
6.  Computer Program in Microfiche (*Appendix*)
7.  Nucleotide and/or Amino Acid Sequence Submission (*if applicable, all must be included*)
  - a.  Paper Copy
  - b.  Computer Readable Copy (*identical to computer copy*)
  - c.  Statement Verifying Identical Paper and Computer Readable Copy

**Accompanying Application Parts**

8.  Assignment Papers (*cover sheet & document(s)*)
9.  37 CFR 3.73(B) Statement (*when there is an assignee*)
10.  English Translation Document (*if applicable*)
11.  Information Disclosure Statement/PTO-1449  Copies of IDS Citations
12.  Preliminary Amendment
13.  Acknowledgment postcard
14.  Certificate of Mailing

First Class  Express Mail (*Specify Label No.*): EE691514962US

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## Accompanying Application Parts (Continued)

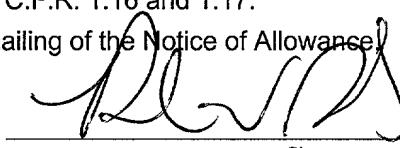
15.  Certified Copy of Priority Document(s) (*if foreign priority is claimed*)
16.  Additional Enclosures (*please identify below*):

## Fee Calculation and Transmittal

### CLAIMS AS FILED

| For  | #Filed                   | #Allowed | #Extra | Rate                    | Fee      |
|--|--------------------------|----------|--------|-------------------------|----------|
| <b>Total Claims</b>                                    | 9                        | - 20 =   | 0      | x \$18.00               | \$0.00   |
| <b>Indep. Claims</b>                                   | 1                        | - 3 =    | 0      | x \$78.00               | \$0.00   |
| <b>Multiple Dependent Claims (check if applicable)</b> | <input type="checkbox"/> |          |        |                         | \$0.00   |
|  |                          |          |        | <b>BASIC FEE</b>        | \$760.00 |
| <b>OTHER FEE (specify purpose)</b>                     |                          |          |        |                         | \$0.00   |
|  |                          |          |        | <b>TOTAL FILING FEE</b> | \$760.00 |

- A check in the amount of \_\_\_\_\_ to cover the filing fee is enclosed.  
 The Commissioner is hereby authorized to charge and credit Deposit Account No. **19-3150** as described below. A duplicate copy of this sheet is enclosed.
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 Charge the issue fee set in 37 C.F.R. 1.18 at the mailing of the Notice of Allowance pursuant to 37 C.F.R. 1.311(b).



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Dated: December 21, 1999

cc:

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## A CATALYTIC CRACKING PROCESS USING A MODIFIED MESOPOROUS ALUMINOPHOSPHATE MATERIAL

10

### BACKGROUND OF THE INVENTION

#### A. Field of the Invention

This invention relates to a catalytic cracking process using a mesoporous aluminophosphate material modified with at least one element selected from zirconium, cerium, lanthanum, manganese, cobalt, zinc, and vanadium. Such materials have high surface area and excellent thermal and hydrothermal stability, with a relatively narrow pore size distribution in the mesoporous range.

#### B. Description of the Prior Art

Amorphous metallophosphates are known and have been prepared by various techniques. One such material is described in U.S. Patent No. 4,767,733. This patent describes rare earth aluminum phosphate materials, which, after calcination, have a relatively broad pore size distribution with a large percentage of pores greater than 150 Å. The typical pore size distribution is as follows:

|    | <u>Pore Size</u> | <u>Volume Percent</u> |
|----|------------------|-----------------------|
| 25 | 50 to 100 Å      | 5 to 20 %             |
|    | 100 to 150 Å     | 10 to 35 %            |
|    | 150 to 200 Å     | 15 to 50 %            |
|    | 200 to 400 Å     | 10 to 50 %            |

U.S. Patent Nos. 4,743,572 and 4,834,869 describe magnesia-alumina-aluminum phosphate support materials prepared using organic cations (e.g., tertiary or tetraalkylammonium or phosphonium cations) to control the pore size distribution. When organic cations are used in the synthesis, the resulting materials have a narrow pore size distribution in the range from 30 to 100 Å. When they are not used, the pore size is predominantly greater than 200 Å. U.S. Patent No. 4,179,358 also describes magnesium-alumina-aluminum phosphate materials, materials described as having excellent thermal stability.

5       The use of aluminophosphates in cracking catalysts is known. For example, U.S.  
Patent No. 4,919,787 describes the use of porous, rare earth oxide, alumina, and  
aluminum phosphate precipitates for catalytic cracking. This material was used as part of  
a cracking catalyst, where it acted as a metal passivating agent. The use of a magnesia-  
alumina-aluminum phosphate supported catalyst for cracking gasoline feedstock is  
10 described in U.S. Patent No. 4,179,358. Additionally, a process for catalytic cracking  
high-metals-content-charge stocks using an alumina-aluminum phosphate-silica-zeolite  
catalyst is described in U.S. Patent No. 4,158,621.

15      There remains a need in the art for highly stable aluminophosphate materials for  
use in catalytic cracking processes, as well as for simple, safe processes for producing  
these materials. The aluminophosphate materials preferably possess excellent  
hydrothermal and acid stability with uniform pore sizes in the mesoporous range, and  
provide increased gasoline yields with increased butylene selectivity in C<sub>4</sub><sup>-</sup> gas.

## SUMMARY OF THE INVENTION

20      This invention resides in a process for catalytic cracking of a hydrocarbon  
feedstock comprising contacting the feedstock with a catalyst composition comprising a  
mesoporous aluminophosphate material which comprises a solid aluminophosphate  
composition modified with at least one element selected from zirconium, cerium,  
lanthanum, manganese, cobalt, zinc, and vanadium, wherein the mesoporous  
25     aluminophosphate material has a specific surface of at least 100 m<sup>2</sup>/g, an average pore  
diameter less than or equal to 100 Å, and a pore size distribution such that at least 50% of  
the pores have a pore diameter less than 100 Å.

Preferably, the mesoporous aluminophosphate material has an average pore  
diameter of 30 to 100 Å.

30      Preferably, the catalyst composition also comprises a primary catalytically active  
cracking component.

Preferably, the primary catalytically active cracking component comprises a large  
pore molecular sieve having a pore size greater than about 7 Angstrom.

5

## DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for converting feedstock hydrocarbon compounds to product hydrocarbon compounds of lower molecular weight than the feedstock hydrocarbon compounds. In particular, the present invention provides a process for catalytically cracking a hydrocarbon feed to a mixture of products comprising gasoline and distillate, in which the gasoline yield is increased and the sulfur content of the gasoline and distillate is reduced. Catalytic cracking units which are amenable to the process of the invention operate at temperatures from about 200°C to about 870°C and under reduced, atmospheric or superatmospheric pressure. The catalytic process can be either fixed bed, moving bed or fluidized bed and the hydrocarbon flow may be either concurrent or countercurrent to the catalyst flow. The process of the invention is particularly applicable to the Fluid Catalytic Cracking (FCC) or Thermoform Catalytic Cracking (TCC) processes.

The TCC process is a moving bed process and uses a catalyst in the shape of pellets or beads having an average particle size of about one-sixty-fourth to one-fourth inch. Active, hot catalyst beads progress downwardly cocurrent with a hydrocarbon charge stock through a cracking reaction zone. The hydrocarbon products are separated from the coked catalyst and recovered, and the catalyst is recovered at the lower end of the zone and regenerated. Typically TCC conversion conditions include an average reactor temperature of about 450°C to about 510°C; catalyst/oil volume ratio of about 2 to about 7; reactor space velocity of about 1 to about 2.5 vol./hr./vol.; and recycle to fresh feed ratio of 0 to about 0.5 (volume).

The process of the invention is particularly applicable to fluid catalytic cracking (FCC), which uses a cracking catalyst which is typically a fine powder with a particle size of about 10 to 200 microns. This powder is generally suspended in the feed and propelled upward in a reaction zone. A relatively heavy hydrocarbon feedstock, e.g., a gas oil, is admixed with the cracking catalyst to provide a fluidized suspension and cracked in an elongated reactor, or riser, at elevated temperatures to provide a mixture of lighter hydrocarbon products. The gaseous reaction products and spent catalyst are discharged from the riser into a separator, e.g., a cyclone unit, located within the upper section of an enclosed stripping vessel, or stripper, with the reaction products being conveyed to a

5 product recovery zone and the spent catalyst entering a dense catalyst bed within the lower section of the stripper. In order to remove entrained hydrocarbons from the spent catalyst prior to conveying the latter to a catalyst regenerator unit, an inert stripping gas, e.g., steam, is passed through the catalyst bed where it desorbs such hydrocarbons conveying them to the product recovery zone. The fluidizable catalyst is continuously  
10 circulated between the riser and the regenerator and serves to transfer heat from the latter to the former thereby supplying the thermal needs of the cracking reaction which is endothermic.

Typically, FCC conversion conditions include a riser top temperature of about 500°C to about 595°C, preferably from about 520°C to about 565°C, and most preferably  
15 from about 530°C to about 550°C; catalyst/oil weight ratio of about 3 to about 12, preferably about 4 to about 11, and most preferably about 5 to about 10; and catalyst residence time of about 0.5 to about 15 seconds, preferably about 1 to about 10 seconds.

The hydrocarbon feedstock to be cracked may include, in whole or in part, a gas oil (e.g., light, medium, or heavy gas oil) having an initial boiling point above 204°C, a 50  
20 % point of at least 260°C and an end point of at least 315°C. The feedstock may also include vacuum gas oils, thermal oils, residual oils, cycle stocks, whole top crudes, tar sand oils, shale oils, synthetic fuels, heavy hydrocarbon fractions derived from the destructive hydrogenation of coal, tar, pitches, asphalts, hydrotreated feedstocks derived from any of the foregoing, and the like. As will be recognized, the distillation of higher  
25 boiling petroleum fractions above about 400°C must be carried out under vacuum in order to avoid thermal cracking. The boiling temperatures utilized herein are expressed for convenience in terms of the boiling point corrected to atmospheric pressure. Resids or deeper cut gas oils with high metals contents can also be cracked using the process of the invention.

30 The process of the invention uses a catalyst composition comprising a mesoporous aluminophosphate material modified with at least one element selected from zirconium, cerium, lanthanum, manganese, cobalt, zinc, and vanadium. "Mesoporous," as used in this patent application, means a material having pores with diameters in the approximate range 30-100 Å.

5 Various important properties of the aluminophosphate materials used in the process of the invention have been identified. In particular, the materials should have a specific surface area of at least 100 m<sup>2</sup>/g, preferably at least 125 m<sup>2</sup>/g, and most advantageously at least 175 m<sup>2</sup>/g. Additionally, the materials should have an average pore diameter less than or equal to 100 Å, preferably less than 80 Å, and most advantageously 10 less than 60 Å.

Pore size distribution and pore volume provide other measures of the porosity of a material. In the modified aluminophosphate materials used in this invention, 50% or more of the pores have a diameter less than 100 Å, more preferably 60% or more of the pores have a diameter less than 100 Å, and most preferably, 80% or more of the pores have a diameter less than 100 Å. With respect to the pore volume, the aluminophosphate materials used in the process of the invention preferably have a pore volume in the range from 0.10 cc/g to 0.75 cc/g, and more preferably within the range of 0.20 to 0.60 cc/g.

The mesoporous aluminophosphate materials used in the process of the invention are synthesized using inorganic reactants, water and aqueous solutions and in the absence of organic reagents or solvents. This feature simplifies production and waste disposal. Synthesis involves providing an aqueous solution that contains a phosphorus component (e.g., phosphoric acid, phosphate salts such as ammonium phosphate which can be monobasic, dibasic or tribasic salt); an inorganic aluminum containing component (e.g., sodium aluminate, aluminum sulfate, or combinations of these materials); and an inorganic modifying component containing at least one element selected from zirconium, cerium, lanthanum, iron, manganese, cobalt, zinc, and vanadium. Typically, the molar ratios of the starting materials are as follows:

|    | <u>Component</u>              | <u>Useful</u> | <u>Preferred</u> |
|----|-------------------------------|---------------|------------------|
| 30 | Phosphorus component          | 0.02-0.90     | 0.05-0.85        |
|    | Aluminum containing component | 0.02-0.90     | 0.05-0.85        |
|    | Inorganic modifying component | 0.01-0.50     | 0.02-0.40        |

After thoroughly mixing the ingredients, the pH of the aqueous solution is 35 adjusted, with an acid or base, into the range of about 7 to about 12 so that a solid

5 material (e.g., a homogeneous gel) forms in and precipitates from the solution. After pH adjustment, the aqueous solution may be exposed to hydrothermal or thermal treatment at about 100°C to about 200°C to further facilitate uniform pore formation. After formation, the solid material, which includes the desired aluminophosphate material, can be recovered by any suitable method known in the art, e.g., by filtration. The filtered cake is then  
10 washed with water to remove any trapped salt, and then may be contacted with a solution containing ammonium salt or acid to exchange out the sodium ions. Such reduction in the sodium level of is found to increase the hydrothermal stability of the aluminophosphate material. Typically, the sodium level of the final aluminophosphate material should less than 1.0 wt% Na. After washing and optional exchange, the solid material is dried and  
15 calcined.

Although any suitable inorganic modifying component can be used in synthesizing the mesoporous aluminophosphate materials used in the process of the invention, preferably it is a sulfate or a nitrate of zirconium, cerium, lanthanum, manganese, cobalt, zinc, or vanadium.

20 In the process of the invention, the modified aluminophosphate material is used in the cracking catalyst, preferably as a support in combination with a primary cracking catalyst component and an activated matrix. Other conventional cracking catalyst materials, such as additive catalysts, binding agents, clays, alumina, silica-alumina, and the like, can also be included as part of the cracking catalyst. Typically, the weight ratio of  
25 the modified aluminophosphate material to the primary cracking catalyst component is about 0.01 to 0.5, preferably 0.02 to 0.15.

The primary cracking component may be any conventional large-pore molecular sieve having cracking activity and a pore size greater than about 7 Angstrom including zeolite X (U.S. Patent 2,882,442); REX; zeolite Y (U.S. Patent 3,130,007); Ultrastable Y  
30 zeolite (USY) (U.S. Patent 3,449,070); Rare Earth exchanged Y (REY) (U.S. Patent 4,415,438); Rare Earth exchanged USY (REUSY); Dealuminated Y (DeAl Y) (U.S. Patent 3,442,792; U.S. Patent 4,331,694); Ultrahydrophobic Y (UHPY) (U.S. Patent 4,401,556); and/or dealuminated silicon-enriched zeolites, e.g., LZ-210 (U.S. Patent 4,678,765). Preferred are higher silica forms of zeolite Y. Zeolite ZK-5 (U.S. Patent  
35 3,247,195);, zeolite ZK-4 (U.S. Patent 3,314,752); ZSM-20 (U.S. Patent 3,972,983);

5 zeolite Beta (U.S. Patent 3,308,069) and zeolite L (U.S. Patents 3,216,789; and  
4,701,315). Naturally occurring zeolites such as faujasite, mordenite and the like may also  
be used. These materials may be subjected to conventional treatments, such as  
impregnation or ion exchange with rare earths to increase stability. The preferred large  
pore molecular sieve of those listed above is a zeolite Y, more preferably an REY, USY or  
10 REUSY.

Other suitable large-pore crystalline molecular sieves include pillared silicates  
and/or clays; aluminophosphates, e.g., ALPO4-5, ALPO4-8, VPI-5;  
silicoaluminophosphates, e.g., SAPO-5, SAPO-37, SAPO-31, SAPO-40; and other metal  
aluminophosphates. These are variously described in U.S. Patents 4,310,440; 4,440,871;  
15 4,554,143; 4,567,029; 4,666,875; 4,742,033; 4,880,611; 4,859,314; and 4,791,083.

The cracking catalyst may also include an additive catalyst in the form of a medium  
pore zeolite having a Constraint Index (which is defined in U.S Patent No. 4,016,218) of  
about 1 to about 12. Suitable medium pore zeolites include ZSM-5 (U.S. Patent  
3,702,886 and Re. 29,948); ZSM-11 (U.S. Patent 3,709,979); ZSM-12 (U.S. Patent  
20 4,832,449); ZSM-22 (U.S. Patent 4,556,477); ZSM-23 (U.S. Patent 4,076,842); ZSM-35  
(U.S. Patent 4,016,245); ZSM-48 (U.S. Patent 4,397,827); ZSM-57 (U.S. Patent  
4,046,685); PSH-3 (U.S. Patent 4,439,409); and MCM-22 (U.S. Patent 4,954,325) either  
alone or in combination. Preferably, the medium pore zeolite is ZSM-5.

The invention will now be more particularly described with reference to the  
25 following Examples. In the Examples, pore size distributions are measured by a N<sub>2</sub>  
desorption process based on ASTM method D4641 and pore volumes are measured by a  
N<sub>2</sub> adsorption process based on ASTM method D4222, which documents are entirely  
incorporated herein by reference. The pore volume and pore size distribution data  
reported herein correspond to pores ranging from approximately 14 to 1000 Å in radius,  
30 and do not include any microporous pores which have typically less than 14 Å in radius.

## **EXAMPLE 1 - Zirconium Aluminophosphate**

### **A. Production of the Support Material**

A zirconium modified aluminophosphate material was prepared by mixing  
35 together, at 40° C, 1700 grams of water, 29 grams of concentrated phosphoric acid, 133

5 grams of zirconium sulfate, and 170 grams of sodium aluminate. In this mixture, the zirconium/aluminum/phosphorus molar ratio was 0.35/0.5/0.15. After thoroughly mixing these ingredients, the pH of the solution was adjusted to 11 using ammonium hydroxide. The resulting mixture was transferred to a polypropylene bottle and placed in a steam box (100° C) for 48 hours. The mixture was then filtered to separate the solid material from  
10 the liquid, and the solid material was washed to provide a wet cake, a portion of which was dried at about 85° C (another portion of this washed material was used in the following test for measuring its hydrothermal stability). A portion of the dried solid material was calcined in air at 540° C for six hours. The resulting zirconium aluminophosphate material had the following properties and characteristics:

15

|    | <u>Elemental Analysis</u>            | <u>Weight Percent</u> |
|----|--------------------------------------|-----------------------|
|    | Zr                                   | 26.4                  |
|    | Al                                   | 24.3                  |
|    | P                                    | 4.0                   |
| 20 | Surface Area - 175 m <sup>2</sup> /g |                       |
|    | Average pore diameter - 41 Å         |                       |
|    | Pore volume - 0.21 cc/g              |                       |

|    | <u>Pore Size Distribution</u> | <u>Desorption, %</u> |
|----|-------------------------------|----------------------|
| 25 | < 50 Å                        | 80%                  |
|    | 50 - 100 Å                    | 10%                  |
|    | 100 - 150 Å                   | 5%                   |
|    | > 150 Å                       | 5%.                  |

30 **B. Hydrothermal Stability Test**

A portion of the wet cake from Example 1A above was slurried with deionized (DI) water (20 g DI water per g of ZrAlPO<sub>x</sub>). The pH of the slurry was adjusted to 4.0 by adding concentrated HCl solution while stirring for 15 minutes. Then the cake was filtered and washed until it was free of residual chloride. The resultant material was dried at 120° C overnight and then air calcined at 540° C for three hours. One portion of this  
35

5 calcined material was steamed (100% atmospheric pressure steam) at 815° C for 2 hours, and another portion was steamed at 815° C for 4 hours. The surface area of the calcined and steamed materials were as follows:

|    | <u>Material</u>     | <u>Surface Area, m<sup>2</sup>/g</u> |
|----|---------------------|--------------------------------------|
| 10 | Calcined only       | 227                                  |
|    | Steamed for 2 hours | 85                                   |
|    | Steamed for 4 hours | 68                                   |

These results demonstrate that the zirconium aluminophosphate material according to the invention is hydrothermally stable and maintains about 30% or more of its surface 15 area under the severe steam deactivating conditions, such as would be experienced in a FCC regenerator. It will also be seen that sodium removal resulting from the acid exchange increased the surface area of the base air calcined material from 175 m<sup>2</sup>/g for the product of Example 1A to 227 m<sup>2</sup>/g for the product of Example 1B.

20 **EXAMPLE 2 - Cerium Aluminophosphate**

**A. Production of the Support Material**

A cerium modified aluminophosphate material was prepared by mixing together, at 40° C, 2100 grams of water, 45 grams of concentrated phosphoric acid, 133 grams of cerium sulfate, 75 grams of concentrated sulfuric acid, and 760 grams of sodium aluminate. In this mixture, the cerium/aluminum/phosphorus molar ratio was 1/8/1. After thoroughly mixing these ingredients, the pH of the solution was adjusted to 7 using 50% sulfuric acid. The resulting mixture was transferred to a polypropylene bottle and placed in a steam box (100° C) for 48 hours. The mixture was then filtered to separate the solid material from the liquid, and the solid material was washed to provide a wet cake, a 25 portion of which was dried at about 85° C (another portion of this washed material was used in the following hydrothermal stability test). A portion of this solid material was calcined in air at 540° C for six hours. The resulting cerium aluminophosphate material had the following properties and characteristics:

|   |                           |                       |
|---|---------------------------|-----------------------|
| 5 | <u>Elemental Analysis</u> | <u>Weight Percent</u> |
|   | Ce                        | 8.6                   |
|   | Al                        | 36.2                  |
|   | P                         | 1.6                   |

Surface Area - 272 m<sup>2</sup>/g

10 Average pore diameter - 65 Å

Pore volume - 0.50 cc/g

|    | <u>Pore Size Distribution</u> | <u>Desorption, %</u> |
|----|-------------------------------|----------------------|
|    | < 50 Å                        | 44%                  |
| 15 | 50 - 100 Å                    | 20%                  |
|    | 100 - 150 Å                   | 12%                  |
|    | > 150 Å                       | 24%.                 |

### B. Hydrothermal Stability Test

20 A portion of the wet cake from Example 2A above was slurried with deionized (DI) water (20 g DI water per g of CeAlPO<sub>x</sub>). The pH of the slurry was adjusted to 4.0 by adding concentrated HCl solution while stirring for 15 minutes. Then the cake was filtered and washed until it was free of residual chloride. The resultant material was dried at 120° C overnight and then air calcined at 540° C for three hours. One portion of this  
 25 calcined material was steamed (100% atmospheric pressure steam) at 815° C for 2 hours, and another portion was steamed at 815° C for 4 hours. The surface area of these calcined and steamed materials were as follows:

|    | <u>Material</u>     | <u>Surface Area, m<sup>2</sup>/g</u> |
|----|---------------------|--------------------------------------|
| 30 | Calcined only       | 272                                  |
|    | Steamed for 2 hours | 138                                  |
|    | Steamed for 4 hours | 143                                  |

These results demonstrate that the cerium aluminophosphate material according to the invention is hydrothermally stable and maintains greater than 50% of its surface area under  
 35 these severe steam deactivating conditions.

5

**EXAMPLE 3 - Cerium Aluminophosphate**

Another cerium modified aluminophosphate material was prepared by mixing together, at 40° C, 2100 grams of water, 360 grams of concentrated phosphoric acid, 135 grams of cerium sulfate, and 100 grams of aluminum sulfate. In this mixture, the cerium/aluminum/phosphorus molar ratio was 1/1/8. After thoroughly mixing these ingredients, the pH of the solution was adjusted to 7 using ammonium hydroxide. The resulting mixture was transferred to a polypropylene bottle and placed in a steam box (100° C) for 48 hours. The mixture was then filtered to separate the solid material from the liquid, and the solid material was washed and dried at about 85° C. This solid material was calcined in air at 540° C for six hours. The resulting cerium aluminophosphate material had the following properties and characteristics:

| <u>Elemental Analysis</u>            | <u>Weight Percent</u> |
|--------------------------------------|-----------------------|
| Ce                                   | 31.4                  |
| Al                                   | 5.5                   |
| P                                    | 21.0                  |
| Surface Area - 133 m <sup>2</sup> /g |                       |
| Average pore diameter - 93 Å         |                       |
| Pore volume - 0.31 cc/g              |                       |

25

| <u>Pore Size Distribution</u> | <u>Desorption, %</u> |
|-------------------------------|----------------------|
| < 50 Å                        | 33%                  |
| 50 - 100 Å                    | 18%                  |
| 100 - 150 Å                   | 12%                  |
| > 150 Å                       | 27%.                 |

30

**EXAMPLE 4 - Lanthanum Aluminophosphate**

A lanthanum modified aluminophosphate material was prepared as follows. A first solution was prepared by mixing together 2500 grams of water, 90 grams of concentrated phosphoric acid, and 260 grams of lanthanum nitrate. A second solution was prepared by

5 combining 1670 grams of water and 600 grams of sodium aluminate. These two solutions  
were combined with stirring. The lanthanum/aluminum/phosphorus molar ratio of this  
mixture was 1/8/1. After thoroughly mixing these solutions, the pH of the resulting  
mixture was adjusted to 12 by adding 150 grams of sulfuric acid. The resulting mixture  
was then transferred to a polypropylene bottle and placed in a steam box (100° C) for 48  
10 hours. Thereafter, the mixture was filtered to separate the solid material from the liquid,  
and the solid material was washed and dried at about 85° C. This solid material was  
calcined in air at 540° C for six hours. The resulting lanthanum aluminophosphate material  
had the following properties and characteristics:

| 15 | <u>Elemental Analysis</u>            | <u>Weight Percent</u> |
|----|--------------------------------------|-----------------------|
|    | La                                   | 16.6                  |
|    | Al                                   | 29.8                  |
|    | P                                    | 4.8                   |
| 20 | Surface Area - 123 m <sup>2</sup> /g |                       |
|    | Average pore diameter - 84 Å         |                       |
|    | Pore volume - 0.26 cc/g              |                       |
| 25 | <u>Pore Size Distribution</u>        | <u>Desorption, %</u>  |
|    | < 50 Å                               | 32%                   |
|    | 50 - 100 Å                           | 56%                   |
|    | 100 - 150 Å                          | 10%                   |
|    | > 150 Å                              | < 5%.                 |

#### **EXAMPLE 5 - Manganese Aluminophosphate**

A manganese modified aluminophosphate material was prepared by mixing  
30 together 2100 grams of water, 45 grams of concentrated phosphoric acid, 68 grams of  
manganese sulfate, and 760 grams of aluminum sulfate. In this mixture, the  
manganese/aluminum/phosphorus molar ratio was 1/8/1. After thoroughly mixing these  
ingredients, the pH of the solution was adjusted to 11 by adding ammonium hydroxide.  
The resulting mixture was transferred to a polypropylene bottle and placed in a steam box  
35 (100° C) for 48 hours. The mixture was then filtered to separate the solid material from

5 the liquid, and the solid material was washed and dried at about 85°C. The solid material  
was re-slurried with deionized water (20 cc of DI water/g of MnAlPO<sub>x</sub>) and the pH of the  
slurry was adjusted to 4.0 or slightly below with a concentrated HCl solution. The pH  
was maintained for 15 minutes and filtered to separate the solid material from the liquid.  
The filter cake was washed thoroughly with 70°C DI water until the washed solution is  
10 free of chloride anion, dried overnight at 120 °C, and then calcined in air at 540°C for six  
hours. The resulting manganese aluminophosphate material had the properties and  
characteristics listed in Table 1.

#### **EXAMPLE 6 - Zinc Aluminophosphate**

15 A zinc modified aluminophosphate material was prepared by mixing together 2100  
grams of water, 45 grams of concentrated phosphoric acid, 115 grams of zinc sulfate, 75  
grams of concentrated sulfuric acid, and 760 grams of sodium aluminate. In this mixture,  
the zinc/aluminum/phosphorus molar ratio was 1/8/1. After thoroughly mixing these  
ingredients, the pH of the solution was adjusted to 11 by adding 50% sulfuric acid. The  
20 resulting mixture was transferred to a polypropylene bottle and placed in a steam box  
(100°C) for 48 hours. The mixture was then filtered to separate the solid material from  
the liquid, and the solid material was washed and dried at about 85°C. The solid material  
was re-slurried with deionized water (20 cc of DI water/g of ZnAlPO<sub>x</sub>) and the pH of the  
slurry was adjusted to 4.0 or slightly below with a concentrated HCl solution. The pH  
25 was maintained for 15 minutes and filtered to separate the solid material from the liquid.  
The filter cake was washed thoroughly with 70°C DI water, dried overnight at 120 °C, and  
then calcined in air at 540°C for six hours. The resulting zinc aluminophosphate material  
had the properties and characteristics listed in Table 1.

30 **EXAMPLE 7 (Comparative)- Iron Aluminophosphate**

A solution was prepared by mixing 1700 grams of water, 65 grams of concentrated  
phosphoric acid, 200 grams of ferrous sulfate, and 110 grams of aluminum sulfate. The  
molar ratio of the iron/aluminum/phosphorous was 0.34/0.33/0.33. The pH of the  
product was adjusted to 7 with the addition of concentrated ammonium hydroxide. The  
35 material was then filtered and washed and dried at ~85°C. A portion of the material was

- 5 air calcined to 540°C for six hours. The resulting iron aluminophosphate material had the properties and characteristics listed in Table 1.

**Table 1**

|   | <u>ZnAlPO<sub>x</sub></u><br><u>Example 5</u><br><u>Invention</u> | <u>MnAlPO<sub>x</sub></u><br><u>Example 6</u><br><u>Invention</u> | <u>FeAlPO<sub>x</sub></u><br><u>Example 7</u><br><u>Comparative</u> |
|---|---|---|---|
| <u>Calcined Acid Form</u>                                 |   |   |   |
| Metal loading, wt%  | 4.2% Zn   | 5.7% Mn   | 21% Fe  |
| Al <sub>2</sub> O <sub>3</sub> , wt%                      | -   | -   | 12.2  |
| P, wt%  | -   | -   | 12.4  |
| Na, wt%   | 0.22  | 0.08  | 0.009   |
| Surface area, m <sup>2</sup> /g                           | 314   | 244   | 109   |
| Average pore diameter (Å)                                 | 50  | 44  | 202   |
| Pore volume (>14Å), cc/g                                  | 0.37  | 0.26  | 0.55  |
| Pore size distribution, %                                 |   |   |   |
| <50 Å   | 39  | 75  | 4   |
| 50-100 Å  | 17  | 23  | 12  |
| 100-150 Å   | 9   | 1   | 15  |
| >150 Å  | 35  | 1   | 69  |
| <u>Steam Deactivated Catalyst<br/>(1500 °F for 4 hrs)</u> |   |   |   |
| Surface area, m <sup>2</sup> /g                           | 155   | 103   | 6   |

10

The results in Table 1 show that ZnAlPO<sub>x</sub> and MnAlPO<sub>x</sub> of the invention retained a surface area in excess of 100 m<sup>2</sup>/g after severe steaming. However, the FeAlPO<sub>x</sub> with a pore size distribution outside the invention lost almost all of its surface area upon steaming.

15

### EXAMPLE 8 - Cobalt Aluminophosphate

#### Sample A (Invention)

A solution was prepared by mixing 500 grams of water, 45 grams of concentrated phosphoric acid, 117 grams of cobalt nitrate and 75 grams of concentrated sulfuric acid.

20

Another solution was prepared containing 1600 grams of water and 300 grams of sodium aluminate. These two solutions were combined with stirring. The molar ratio of the

5 cobalt/aluminum/phosphorous was 1/8/1. The pH of the mixture was adjusted to 9 with  
the addition of 50% solution of sulfuric acid. The resulting mixture was placed in a  
polypropylene bottle and put in a steam box (100°C) for 48 hours. The mixture was then  
filtered and the solid residue was washed and dried at ~85°C. A portion of the residue  
was air calcined to 540°C for six hours. The elemental analyses and physical properties  
10 were as follows:

| Element, wt%                    |      |
|---------------------------------|------|
| Co                              | 7.1  |
| Al                              | 25.3 |
| P                               | 3.4  |
| Surface Area, m <sup>2</sup> /g | 145  |

A portion of the above material was exchanged four times with a 0.1N solution of  
ammonium nitrate and the resulting material was then filtered and washed and dried at  
15 ~85°C. A portion of the material was air calcined to 540°C for six hours. The resulting  
cobalt aluminophosphate material had the properties and characteristics listed in Table 2.

#### Sample B (Invention)

A solution was prepared by mixing 2100 grams of water, 45 grams of concentrated  
20 phosphoric acid, 117 grams of cobalt nitrate, 75 grams of concentrated sulfuric acid, and  
300 grams of sodium aluminate. The molar ratio of the cobalt/aluminum/phosphorous  
was 1/8/1. The pH of the mixture was adjusted to 8 with the addition of 50% solution of  
sulfuric acid. The resulting mixture was placed in a polypropylene bottle and put in a  
steam box (100°C) for 48 hours. The mixture was then filtered and the solid residue was  
25 washed and dried at ~85°C. A portion of the residue was air calcined to 540°C for six  
hours. The elemental analyses and physical properties were as follows:

| Element, wt%                    |      |
|---------------------------------|------|
| Co                              | 6.0  |
| Al                              | 19.2 |
| P                               | 2.6  |
| Surface Area, m <sup>2</sup> /g | 114  |

5

A portion of the above material was exchanged four times with a 0.1N solution of ammonium nitrate and the resulting material was then filtered and washed and dried at ~85°C. A portion of the material was air calcined to 540°C for six hours. The resulting cobalt aluminophosphate material had the properties and characteristics listed in Table 2.

10

### Sample C (Invention)

A cobalt modified aluminophosphate material was prepared in the same manner as for Sample B above, except the pH of the mixture was adjusted to 7 with the addition of 50% solution of sulfuric acid. The elemental analyses and physical properties of the product were as follows:

| Element, wt% |      |
|--------------|------|
| Co           | 6.8  |
| Al           | 19.6 |
| P            | 2.9  |

A portion of the above material was slurried with DI water (20 g DI water per g of CoAlPO<sub>x</sub>). The pH of the slurry was adjusted to 4.0 by adding concentrated HCl solution while stirring for 15 minutes. Then the cake was filtered and washed until it was free of residual chloride. The gel was dried at 120°C for overnight and calcined in air at 538°C for 3 hours. The resulting cobalt aluminophosphate material had the properties and characteristics listed in Table 2.

25      **Sample D (Comparative)**

A cobalt modified aluminophosphate material was prepared by mixing 2100 grams of water, 45 grams of concentrated phosphoric acid, 117 grams of cobalt nitrate, 75 grams of concentrated sulfuric acid, and 300 grams of aluminum sulfate. The molar ratio of the cobalt/aluminum/phosphorous was 1/8/1. The pH of the mixture was adjusted to 11 with the addition of concentrated ammonium hydroxide. The resulting mixture was placed in a polypropylene bottle and put in a steam box (100°C) for 48 hours. The mixture was then filtered and the solid residue was washed and dried at ~85°C. A portion

5 of the residue was air calcined to 540°C for six hours. The elemental analyses and physical properties were as follows:

| Element, wt% |      |
|--------------|------|
| Co           | 10.7 |
| Al           | 27.4 |
| P            | 5.8  |

10 A portion of the above material was slurried with DI water (20 g DI water per g of CoAlPO<sub>x</sub>). The pH of the slurry was adjusted to 4.0 by adding concentrated HCl solution while stirring for 15 minutes. Then the cake was filtered and washed until it was free of residual chloride. The gel was dried at 120°C for overnight and calcined in air at 538°C for 3 hours. The resulting cobalt aluminophosphate material had the properties and characteristics listed in Table 2.

15

### Sample E (Comparative)

A cobalt modified aluminophosphate material was prepared from a solution which was prepared with mixing, containing 1700 grams of water, 29 grams of concentrated phosphoric acid, 213 grams of cobalt nitrate, and 170 grams of aluminum sulfate. The molar ratio of the cobalt/aluminum/phosphorous was 0.35/0.5/0.15. The pH of the mixture was adjusted to 7 with the addition of concentrated ammonium hydroxide. The resulting mixture was placed in a polypropylene bottle and put in a steam box (100°C) for 48 hours. The mixture was then filtered and the solid residue was washed and dried at ~85°C. A portion of the residue was air calcined to 540°C for six hours. The elemental analyses and physical properties were as follows:

| Element, wt% |      |
|--------------|------|
| Co           | 28   |
| Al           | 10.9 |
| P            | 6.3  |

A portion of the above material was slurried with DI water (20 g DI water per g of CoAlPO<sub>x</sub>). The pH of the slurry was adjusted to 4.0 by adding concentrated HCl solution

5 while stirring for 15 minutes. Then the cake was filtered and washed until it was free of residual chloride. The gel was dried at 120°C for overnight and calcined in air at 538°C for 3 hours. The resulting cobalt aluminophosphate material had the properties and characteristics listed in Table 2.

10 **Hydrothermal Stability Test of the CoAlPO<sub>x</sub> Samples**

The hydrothermal stability of each CoAlPO<sub>x</sub> gel was evaluated by steaming the material at 1500°F (815°C) for 4 hours with 100% steam at atmospheric pressure. The results are given in Table 2 below and Figure 1. The results show that Samples A-C, with the average pore size and pore size distribution according to the invention, exhibited 15 excellent hydrothermal stability in that they maintained over 100 m<sup>2</sup>/g surface area even after severe steaming. In contrast, Samples D and E, without the narrowly-defined mesopores structure of the invention, lost nearly all of their surface area upon steaming at 1500°F.

20

**Table 2**

| Sample   | A    | B    | C    | D    | E    |
|--|------|------|------|------|------|
| Calcined Acid Form                               |      |      |      |      |      |
| Co loading, wt%                                  | 6.2  | 7.9  | 10   | 15   | 28   |
| Al <sub>2</sub> O <sub>3</sub> , wt%             | 47.8 | 36   | 51   | 18   | 20   |
| P, wt%   | 3.4  | 2.6  | 4    | 11   | 10   |
| Na, wt%  | 0.49 | 0.28 | 0.05 | 0.01 | 0.01 |
| Surface area, m <sup>2</sup> /g                  | 321  | 247  | 175  | 103  | 82   |
| Average pore diameter (Å)                        | 67   | 74   | 74   | 152  | 108  |
| Pore volume (>14Å), cc/g                         | 0.55 | 0.44 | 0.37 | 0.38 | 0.24 |
| Pore size distribution, %                        |      |      |      |      |      |
| <50 Å  | 38   | 29   | 32   | 8    | 13   |
| 50-100 Å   | 32   | 39   | 27   | 14   | 27   |
| 100-150 Å  | 9    | 11   | 13   | 14   | 19   |
| >150 Å   | 21   | 21   | 28   | 64   | 41   |
| Steam Deactivated Catalyst<br>(1500°F for 4 hrs) |      |      |      |      |      |
| Surface area, m <sup>2</sup> /g                  | 128  | 113  | 111  | 29   | 18   |

5   **EXAMPLE 9 -Vanadium Aluminophosphate**

**Sample F**

A solution was prepared by mixing 2100 grams of water, 45 grams of concentrated phosphoric acid, 87 grams of vanadyl sulfate, 75 grams of concentrated sulfuric acid and 760 grams of sodium aluminate. The molar ratio of the vanadium/aluminum/ phosphorous was 1/8/1. The pH of the mixture was adjusted to 7 with the addition of 50% sulfuric acid. The mixture was then filtered and the solid residue washed and dried at about 85°C. A portion of the dried material was air calcined to 540°C for six hours. The elemental analyses and physical properties of resulting vanadium aluminophosphate material were as follows:

15

| Element, wt%                    |      |
|---------------------------------|------|
| V                               | 3.0  |
| Al                              | 17.0 |
| P                               | 1.7  |
| Surface Area, m <sup>2</sup> /g | 335  |

A further portion of the above dried material was slurried with DI water (20 g DI water per g of VAlPO<sub>x</sub>). The pH of the slurry was adjusted to 4.0 by adding concentrated HCl solution while stirring for 15 minutes. Then the cake was filtered and washed until it was free of residual chloride. The gel was dried at 120°C for overnight and calcined in air at 538°C for 3 hours. The resulting vanadium aluminophosphate material had the properties and characteristics listed in Table 3.

**Sample G**

25   A solution was prepared by mixing 2100 grams of water, 45 grams of concentrated phosphoric acid, 87 grams of vanadyl sulfate, 75 grams of concentrated sulfuric acid and 760 grams of sodium aluminate. The molar ratio of the vanadium/aluminum/ phosphorous was 1/8/1. The pH of the mixture was adjusted to 8 with the addition of 50% solution of sulfuric acid. The elemental analyses and physical properties of the resulting vanadium aluminophosphate material were as follows:

| Element, wt%                    |      |
|---------------------------------|------|
| V                               | 2.1  |
| Al                              | 20.9 |
| P                               | 1.2  |
| Surface Area, m <sup>2</sup> /g | 130  |

5

A further portion of the above dried material was exchanged four times with a 0.1N solution of ammonium nitrate to remove the excess sodium, and the resultant product was then filtered and the residue washed and dried at about 85°C. A portion of the residue was air calcined to 540°C for six hours. The resulting vanadium 10 aluminophosphate material had the properties and characteristics listed in Table 3.

The calcined acid form of each of the VAlPO<sub>x</sub> Samples F and G were subjected to the steam deactivation test described above and the results are summarized in Table 3.

15  
**Table 3**

|   | <i>VAlPO<sub>x</sub></i><br><i>Sample F</i><br><i>Invention</i> | <i>VAlPO<sub>x</sub></i><br><i>Sample G</i><br><i>Invention</i> |
|---|---|---|
| <u>Calcined Acid Form</u>                       |   |   |
| V loading, wt%                                  | 3.0   | 2.1   |
| Al <sub>2</sub> O <sub>3</sub> , wt%            | 39  | 35.6  |
| P, wt%  | 1.2   | 0.3   |
| Na, wt%   | 0.59  | 0.83  |
| Surface area, m <sup>2</sup> /g                 | 317   | 304   |
| Average pore diameter (Å)                       | 53  | 36  |
| Pore volume (>14Å), cc/g                        | 0.42  | 0.27  |
| Pore size distribution, %                       |   |   |
| <50 Å   | 55  | 82  |
| 50-100 Å  | 20  | 10  |
| 100-150 Å                                       | 6   | 2   |
| >150 Å  | 19  | 6   |
| Steam Deactivated Catalyst<br>(1500F for 4 hrs) |   |   |
| Surface area, m <sup>2</sup> /g                 | 81  | 126   |

5        The results in Table 3 show that Samples F and G, with the average pore size and  
pore size distribution according to the invention, exhibited excellent hydrothermal stability.  
Sample G prepared under higher pH conditions exhibited better stability in that it  
maintained over 100 m<sup>2</sup>/g surface area even after severe steaming.

10      **EXAMPLE 10 - Fluid Catalytic Cracking with ZrAlPO<sub>x</sub>**

A.      **Preparation of a ZrAlPO<sub>x</sub> Material**

A thermally stable, high surface area, mesoporous ZrAlPO<sub>x</sub> material was prepared as described above in Example 1. The described wet cake of ZrAlPO<sub>x</sub> was used for the catalyst preparations that follow.

15

B.      **Preparation of a USY/ZrAlPO<sub>x</sub>/Clay Catalyst**

A first catalyst, Catalyst A, was prepared using commercial Na-form USY zeolite with a silica to alumina ratio of 5.4 and a unit cell size of 24.54 Å. The Na-form USY was slurried and ball milled for 16 hours. A wet cake of the ZrAlPO<sub>x</sub> material above was slurried in deionized water, and the pH of the resultant slurry was adjusted to 4 using concentrated HCl. The ZrAlPO<sub>x</sub> material was then filtered, washed, and ball milled for 16 hours.

20

A uniform physical mixture of the milled USY slurry, the milled ZrAlPO<sub>x</sub> slurry, binding agent, and kaolin clay was prepared. The final slurry contained 21% USY, 25% ZrAlPO<sub>x</sub>, 7% binding agent, and 47% clay, on a 100% solids basis. The mixture was spray-dried to fine spherical particles with approximately 70 µ average particle diameter. The sprayed product was then air calcined, followed by ammonium exchange using an ammonium sulfate solution. The exchanged catalyst was further washed with deionized water, dried overnight, and calcined at 538°C for three hours. The properties of the final catalyst are shown in Table 4.

25

C.      **Preparation of a USY/Alumina/Clay Catalyst**

A second catalyst, Catalyst B, was prepared following the procedure in Example 10B, above, except that the ZrAlPO<sub>x</sub> in Catalyst A was replaced with HCl-peptized alumina. The peptized alumina gel was prepared from pseudoboehmite alumina powder

5 that was peptized with HCl solution for 30 minutes (at 12 wt% solids). The properties of Catalyst B also are shown in Table 4.

#### D. Preparation of a USY/ZrAlPO<sub>x</sub>/Alumina/Clay Catalyst

A third catalyst, Catalyst C, was prepared following the procedure in Example 10B, above, except that the amount of ZrAlPO<sub>x</sub> was reduced and part of the clay was 10 replaced with the HCl-peptized alumina used in Example 10C so that the spray dried slurry contained 21% USY, 15% ZrAlPO<sub>x</sub>, 25% alumina, 7% binding agent, and 32% clay, on a 100% solids basis. The final properties of Catalyst C are shown in Table 4.

#### E. Preparation of a USY/ZrAlPO<sub>x</sub>/Alumina/Clay Catalyst

A fourth catalyst, Catalyst D, was prepared following the procedure in Example 15 10D, above, except that the ZrAlPO<sub>x</sub> in Catalyst C was replaced with HCl-peptized ZrAlPO<sub>x</sub> gel, prepared by peptization of wet cake using HCl solution. The properties of Catalyst D also are shown in Table 4.

Before evaluating the catalysts for performance on a pilot unit for catalytic cracking, each catalyst was deactivated at 1450° F and 35 psig for 20 hours using 50% 20 steam and 50% air. The surface areas of the steamed catalysts are shown in Table 4.

**TABLE 4**

|                                       | Catalyst A                             | Catalyst B                             | Catalyst C  | Catalyst D   |
|---------------------------------------|--|--|---|--|
| Compositional Feature                 | 25% ZrAlPO <sub>x</sub> and No Alumina | 25% Alumina and No ZrAlPO <sub>x</sub> | 15% Ball Milled ZrAlPO <sub>x</sub> (Replaced Part of Clay) and 25% Alumina | 15% Peptized ZrAlPO <sub>x</sub> (Replaced Part of Clay) and 25% Alumina |
| Calcined Catalyst Properties          |  |  |   |  |
| Rare Earth wt.%                       | 1.7                                    | 1.9                                    | 1.9   | 1.8  |
| Na wt.%                               | 0.1                                    | 0.1                                    | 0.1   | 0.1  |
| SiO <sub>2</sub> wt.%                 | 37.1                                   | 36.7                                   | 29.6  | 30.3   |
| Al <sub>2</sub> O <sub>3</sub> wt.%   | 42.5                                   | 52.0                                   | 51.6  | 54.2   |
| Surface Area m <sup>2</sup> /g        | 221                                    | 222                                    | 255   | 256  |
| Steam Deactivated Catalyst Properties |  |  |   |  |
| Surface Area m <sup>2</sup> /g        | --                                     | 123                                    | 122   | 120  |

5      **F.      Catalytic Cracking Process**

Catalysts B through D were compared for catalytic cracking activity in a fixed-fluidized-bed ("FFB") reactor at 935°F, using a 1.0 minute catalyst contact time on a Arab Light Vacuum Gas Oil. The feedstock properties are shown in Table 5 below:

10

**TABLE 5**

| Charge Stock Properties | Vacuum Gas Oil |
|-------------------------|----------------|
| Gravity at 60° F        | 0.9010         |
| Refractive Index        | 1.50084        |
| Aniline Point, ° F      | 164            |
| CCR, wt.%               | 0.90           |
| Hydrogen, wt.%          | 11.63          |
| Sulfur, wt.%            | 2.8            |
| Nitrogen, ppm           | 990            |
| Basic nitrogen, ppm     | 250            |
| Distillation            |                |
| IBP, ° F                | 536            |
| 50 wt.%, ° F            | 868            |
| 99.5 wt.%, ° F          | 1170           |

These catalysts were then used in the FFB pilot plant. The catalyst performances are summarized in Table 6, where product selectivity was interpolated to a constant conversion, 65 wt.% conversion of feed to 430° F material.

TABLE 6

|                        | Catalyst B                   | Catalyst C                               | Catalyst D                            |
|------------------------|------------------------------|--|---------------------------------------|
| Matrix                 | No Added ZrAlPO <sub>x</sub> | + 15% Ball Milled<br>ZrAlPO <sub>x</sub> | + 15% Peptized<br>ZrAlPO <sub>x</sub> |
| Conversion, wt.%       | 65                           | 65                                       | 65                                    |
| Cat/Oil                | 3.8                          | 3.3                                      | 3.6                                   |
| $C_5^+$ Gasoline, wt.% | 39.6                         | 42.1                                     | 42.4                                  |
| LFO, wt.%              | 25.4                         | 25.6                                     | 25.5                                  |
| HFO, wt.%              | 9.6                          | 9.4                                      | 9.5                                   |
| Coke, wt.%             | 5.1                          | 5.3                                      | 5.1                                   |
| RON, $C_5^+$ Gasoline  | 88.2                         | 85.7                                     | 85.6                                  |
| $H_2S$ , wt.%          | 1.7                          | 1.8                                      | 1.9                                   |
| $C_1 + C_2$ Gas, wt.%  | 1.8                          | 1.8                                      | 1.7                                   |
| Total $C_3$ Gas, wt.%  | 6.3                          | 4.9                                      | 4.9                                   |
| Total $C_4$ Gas, wt.%  | 10.4                         | 8.9                                      | 8.8                                   |
| $C_3^-$ /total $C_3$   | 0.81                         | 0.80                                     | 0.80                                  |
| $C_4^-$ /total $C_4$   | 0.48                         | 0.48                                     | 0.50                                  |
| $C_4^-$ / $C_3^-$      | 0.98                         | 1.10                                     | 1.13                                  |

The test results in Table 6 demonstrate that incorporation of ZrAlPO<sub>x</sub> into the

10 zeolite matrix resulted in significantly improved gasoline yields (as much as 2.8 wt.%).

This increase in gasoline yields for Catalysts C and D resulted mostly from lower  $C_3$  and  $C_4$  yields. The ZrAlPO<sub>x</sub> matrix "as-is" (Catalyst C) had a slightly higher coke-making tendency, but this tendency was alleviated by HCl peptization of the gel (Catalyst D).

The ZrAlPO<sub>x</sub> matrix has bottoms cracking activity, and a slight decrease in HFO

15 (heavy fuel oil) yield is observed (0.2%). The bottoms yield differences are small for these catalysts, probably because all three catalysts convert nearly all of the crackable heavy ends at this conversion level. One negative aspect of the ZrAlPO<sub>x</sub> containing catalyst is the lower research octane number ("RON") of the produced gasoline, lowered by as much as 2.6.

5        The ZrAlPO<sub>x</sub> containing catalysts increased the H<sub>2</sub>S yield by >10%, suggesting  
that this material may have potential for SO<sub>x</sub> removal and/or gasoline sulfur removal. The  
ZrAlPO<sub>x</sub> containing catalysts increased the butylene selectivity in C<sub>4</sub> gas and the C<sub>4</sub> olefin-  
to-C<sub>3</sub> olefin ratio. The results in Table 6 clearly show that the chemistry of ZrAlPO<sub>x</sub> is  
different from a typical active alumina matrix, which is usually added to improve bottoms  
10 cracking.

#### **EXAMPLE 11 - Fluid Catalytic Cracking with CeAlPO<sub>x</sub>**

##### **A. Preparation of a CeAlPO<sub>x</sub> Material**

15      A thermally stable, high surface area, mesoporous CeAlPO<sub>x</sub> material was prepared  
as described above in Example 2. The wet cake of CeAlPO<sub>x</sub> described above was used for  
the catalyst preparations that follow.

##### **B. Preparation of a USY/CeAlPO<sub>x</sub>/Clay Catalyst**

20      A first catalyst, Catalyst E, was prepared using commercial Na-form USY zeolite  
with a silica to alumina ratio of 5.4 and a unit cell size of 24.54 Å. The Na-form USY was  
slurried and ball milled for 16 hours. A wet cake of the CeAlPO<sub>x</sub> material above was  
25     slurried in deionized water, and the pH of the resultant slurry was adjusted to 4 using  
concentrated HCl. The CeAlPO<sub>x</sub> material was then filtered, washed, and ball milled for 16  
hours.

30      A uniform physical mixture of the milled USY slurry, the milled CeAlPO<sub>x</sub> slurry,  
binding agent, and kaolin clay was prepared. The final slurry contained 21% USY, 25%  
CeAlPO<sub>x</sub>, 7% binding agent, and 47% clay, on a 100% solids basis. The mixture was  
spray-dried to fine spherical particles with approximately 70 µ average particle diameter.  
The sprayed product was then air calcined, followed by ammonium exchange using an  
ammonium sulfate solution. The exchanged catalyst was further washed with deionized  
35     water, dried overnight, and calcined at 538°C for three hours. The properties of the final  
catalyst are shown in Table 7.

##### **C. Preparation of a USY/Alumina/Clay Catalyst**

35      A second catalyst, Catalyst F, was prepared following the procedure in Example  
11B, above, except that the CeAlPO<sub>x</sub> in Catalyst E was replaced with HCl-peptized  
pseudoboehmite alumina. The properties of Catalyst F also are shown in Table 7.

5      **D. Preparation of a USY/CeAlPO<sub>x</sub>/Alumina/Clay Catalyst**

A third catalyst, Catalyst G, was prepared following the procedure in Example 11B, above, except that the amount of CeAlPO<sub>x</sub> was reduced and part of the clay was replaced with the HCl-peptized alumina used in Example 11C so that the spray dried slurry contained 21% USY, 15% CeAlPO<sub>x</sub>, 25% alumina, 7% binding agent, and 32% 10 clay, on a 100% solids basis HCl-peptized pseudoboehmite alumina. The final properties of Catalyst G are shown in Table 7.

**E. Preparation of a USY/CeAlPO<sub>x</sub>/Alumina/Clay Catalyst**

A fourth catalyst, Catalyst H, was prepared following the procedure in Example 11D, above, except that the CeAlPO<sub>x</sub> in Catalyst G was replaced with HCl-peptized 15 CeAlPO<sub>x</sub>. The properties of Catalyst H also are shown in Table 7.

Before evaluating the catalysts for performance on a pilot unit for catalytic cracking, each catalyst was deactivated at 1450° F and 35 psig for 20 hours using 50% steam and 50% air. The surface areas of the steamed catalysts are shown in Table 7.

20

**TABLE 7**

| Compositional Feature                  | Catalyst E                             | Catalyst F  | Catalyst G   | Catalyst H |
|--|--|---|--|------------|
| 25% CeAlPO <sub>x</sub> and No Alumina | 25% Alumina and No CeAlPO <sub>x</sub> | 15% Ball Milled CeAlPO <sub>x</sub> (Replaced Part of Clay) and 25% Alumina | 15% Peptized CeAlPO <sub>x</sub> (Replaced Part of Clay) and 25% Alumina |            |
| Calcined Catalyst Properties           |  |   |  |            |
| Rare Earth wt.%                        | 4.9                                    | 1.9   | 3.7  | 3.5        |
| Na wt.%                                | 0.1                                    | 0.1   | 0.1  | 0.2        |
| SiO <sub>2</sub> wt.%                  | 38.1                                   | 36.7  | 31.0   | 30.6       |
| Al <sub>2</sub> O <sub>3</sub> wt.%    | 46.5                                   | 52.0  | 57.9   | 55.5       |
| Surface Area m <sup>2</sup> /g         | 238                                    | 222   | 249  | 257        |
| Steam Deactivated Catalyst Properties  |  |   |  |            |
| Surface Area m <sup>2</sup> /g         | 90                                     | 123   | 130  | 126        |

**F. Catalytic Cracking Process**

Catalysts E and F were compared for use in a catalytic cracking process using an 25 FFB reactor at 935°F, having a 1.0 minute catalyst contact time using Arab Light Vacuum Gas Oil. The feedstock had the properties described in Table 5 above.

5       The performances of the catalysts are summarized in Table 8, where product selectivity was interpolated to a constant conversion, 65 wt.% conversion of feed to 430° F material.

TABLE 8

10

|  | Deactivated Catalyst E  | Deactivated Catalyst F                       |
|--|-------------------------|--|
| Matrix                                     | 25% CeAlPO <sub>x</sub> | 25% Activated Al <sub>2</sub> O <sub>3</sub> |
| Conversion, wt.%                           | 65                      | 65   |
| Cat/Oil                                    | 4.1                     | 3.8  |
|  |                         |  |
| C <sub>1</sub> + C <sub>2</sub> Gas, wt.%  | 2.0                     | 1.8  |
| Total C <sub>3</sub> Gas, wt.%             | 5.4                     | 6.3  |
| Total C <sub>4</sub> Gas, wt.%             | 9.5                     | 10.4   |
|  |                         |  |
| C <sub>5</sub> <sup>+</sup> Gasoline, wt.% | 40.7                    | 39.6   |
| LFO, wt.%                                  | 25.0                    | 25.4   |
| HFO, wt.%                                  | 10.0                    | 9.6  |
| Coke, wt.%                                 | 5.5                     | 5.1  |
| RON, C <sub>5</sub> <sup>+</sup> Gasoline  | 87.6                    | 88.2   |

The results in Table 8 suggest that the CeAlPO<sub>x</sub> matrix has bottoms cracking activity comparable to that of the activated alumina matrix. The catalysts provided comparable HFO yields. The CeAlPO<sub>x</sub> catalyst shows higher gasoline selectivity (1.1  
15   wt.% yield advantage).

#### G. Product Selectivity Improvement With Addition of CeAlPO<sub>x</sub>

Catalysts G and H were compared with Catalyst F to determine the benefits of adding CeAlPO<sub>x</sub> to an FCC catalyst. An FFB reactor was used with the Arab Light  
20   Vacuum Gas Oil described above in Table 5. The performances of the catalysts are

5 summarized in Table 9, where product selectivity was interpolated to a constant conversion, 65 wt.% conversion of feed to 430° F material.

TABLE 9

|  | Catalyst F                   | Catalyst G                            | Catalyst H                         |
|--|------------------------------|---------------------------------------|------------------------------------|
| Matrix   | No Added CeAlPO <sub>x</sub> | + 15% Ball Milled CeAlPO <sub>x</sub> | + 15% Peptized CeAlPO <sub>x</sub> |
| Conversion, wt.%   | 65                           | 65                                    | 65                                 |
| Cat/Oil  | 3.8                          | 3.6                                   | 3.5                                |
| C <sub>5</sub> <sup>+</sup> Gasoline, wt.%               | 39.6                         | 40.7                                  | 42.0                               |
| LFO, wt.%  | 25.4                         | 25.0                                  | 25.3                               |
| HFO, wt.%  | 9.6                          | 10.0                                  | 9.7                                |
| Coke, wt.%   | 5.1                          | 5.5                                   | 5.2                                |
| RON, C <sub>5</sub> <sup>+</sup> Gasoline                | 88.2                         | 87.8                                  | 85.5                               |
| H <sub>2</sub> S, wt.%                                   | 1.7                          | 1.9                                   | 1.9                                |
| C <sub>1</sub> + C <sub>2</sub> Gas, wt.%                | 1.8                          | 1.8                                   | 1.7                                |
| Total C <sub>3</sub> Gas, wt.%                           | 6.3                          | 5.4                                   | 5.0                                |
| Total C <sub>4</sub> Gas, wt.%                           | 10.4                         | 9.5                                   | 9.1                                |
| C <sub>3</sub> <sup>=</sup> /total C <sub>3</sub>        | 0.81                         | 0.81                                  | 0.80                               |
| C <sub>4</sub> <sup>=</sup> /total C <sub>4</sub>        | 0.48                         | 0.52                                  | 0.49                               |
| C <sub>4</sub> <sup>=</sup> /C <sub>3</sub> <sup>=</sup> | 0.98                         | 1.11                                  | 1.13                               |

10

The test results in Table 9 demonstrate that incorporation of CeAlPO<sub>x</sub> into the matrix resulted in significantly improved gasoline yields (as much as 2.4 wt.%). The increase in gasoline yields for Catalysts G and H resulted mostly from lower C<sub>3</sub> and C<sub>4</sub> yields. The CeAlPO<sub>x</sub> matrix "as-is" (Catalyst G) had a slightly higher coke-making tendency, but this tendency was alleviated by HCl peptization of the gel (Catalyst H).

15

The bottoms yields are comparable for all three catalysts, probably because all three catalysts convert nearly all of the crackable heavy ends at this conversion level. One negative aspect of the CeAlPO<sub>x</sub> containing catalyst is that it lowered the research octane number ("RON") of the produced gasoline by as much as 2.7.

5        The CeAlPO<sub>x</sub> containing catalysts increased the H<sub>2</sub>S yield by >10%, suggesting  
       that this material may have potential for SO<sub>x</sub> removal and/or gasoline sulfur removal. The  
       CeAlPO<sub>x</sub> containing catalysts increased the butylene selectivity in C<sub>4</sub> gas, and the C<sub>4</sub>  
       olefin-to-C<sub>3</sub> olefin ratio. The results in Table 9 clearly show that the chemistry of  
       CeAlPO<sub>x</sub> is different from a typical active alumina matrix, which is usually added to  
 10      improve bottoms cracking.

#### **EXAMPLE 12 - Fluid Catalytic Cracking Evaluation of CoAlPO<sub>x</sub> and VAlPO<sub>x</sub>**

CoAlPO<sub>x</sub> from Example 8 (Sample A) and VAlPO<sub>x</sub> from Example 9 (Sample F)  
       were each pelleted and sized to an average particle size of approximately 70 micrometer  
 15      ( $\mu$ ), then steamed in a muffle furnace at 1500°F for 4 hours to simulate catalyst  
       deactivation in an FCC unit. Ten weight percent of steamed pellets were blended with an  
       equilibrium catalyst from an FCC unit. The equilibrium catalyst has very low metals level  
       (120 ppm V and 60 ppm Ni).

20      The additives were tested for gas oil cracking activity and selectivity using an  
       ASTM microactivity test (ASTM procedure D-3907). The vacuum gas oil feed stock  
       properties are shown in a Table 10 below.

**Table 10**

| <i>Charge Stock Properties</i> | <i>Vacuum Gas Oil</i> |
|--------------------------------|-----------------------|
| API Gravity                    | 26.6                  |
| Aniline Point, °F              | 182                   |
| CCR, wt%                       | 0.23                  |
| Sulfur, wt%                    | 1.05                  |
| Nitrogen, ppm                  | 600                   |
| Basic nitrogen, ppm            | 310                   |
| Ni, ppm                        | 0.32                  |
| V, ppm                         | 0.68                  |
| Fe, ppm                        | 9.15                  |
| Cu, ppm                        | 0.05                  |
| Na, ppm                        | 2.93                  |
| Distillation                   |                       |
| IBP, °F                        | 358                   |
| 50wt%, °F                      | 716                   |
| 99.5%, °F                      | 1130                  |

5

A range of conversions was scanned by varying the catalyst-to-oil ratios and reactions were run at 980°F. Gasoline range product from each material balance was analyzed with a GC equipped with a sulfur detector (AED) to determine the gasoline sulfur concentration. To reduce experimental errors in sulfur concentration associated  
10 with fluctuations in distillation cut point of the gasoline, S species ranging only from thiophene to C4-thiophenes were quantified using the sulfur detector and the sum was defined as "cut-gasoline S". The sulfur level reported for "cut-gasoline S" excludes any benzothiophene and higher boiling S species which were trapped in a gasoline sample due to distillation overlap. Performances of the catalysts are summarized in Table 11, where  
15 the product selectivity was interpolated to a constant conversion, 65wt% or 70wt% conversion of feed to 430°F<sup>-</sup> material.

**Table 11**

|   | <i>Base Case</i> | <i>+ 10% CoAlPO<sub>x</sub></i> | <i>+ 10% VAlPO<sub>x</sub></i> |
|---|------------------|---------------------------------|--------------------------------|
| Conversion, wt%                           | 70               | 70                              | 70                             |
| Cat/Oil                                   | 3.2              | 3.2                             | 3.7                            |
| <br>                                      |                  |                                 |                                |
| H <sub>2</sub> yield, wt%                 | 0.04             | +0.24                           | +0.21                          |
| C <sub>1</sub> + C <sub>2</sub> Gas, wt%  | 1.4              | +0.3                            | +0                             |
| Total C <sub>3</sub> Gas, wt%             | 5.4              | +0.1                            | -0.2                           |
| C <sub>3</sub> <sup>=</sup> yield, wt%    | 4.6              | +0                              | -0.1                           |
| Total C <sub>4</sub> Gas, wt%             | 11.1             | -0.2                            | -0.4                           |
| C <sub>4</sub> <sup>=</sup> yield, wt%    | 5.4              | -0.1                            | +0.1                           |
| iC <sub>4</sub> yield, wt%                | 4.8              | -0.2                            | -0.4                           |
| C <sub>5</sub> <sup>+</sup> Gasoline, wt% | 49.3             | -1.7                            | -0.9                           |
| LFO, wt%                                  | 25.6             | -0.4                            | +0.1                           |
| HFO, wt%                                  | 4.4              | +0.4                            | -0.1                           |
| Coke, wt%                                 | 2.5              | +1.4                            | +1.3                           |
| Cut Gasoline S, PPM                       | 445              | 330                             | 383                            |
| % Reduction in Cut Gasoline S             | Base             | 26.0                            | 13.9                           |
| % Reduction in Gasoline S, Feed Basis     | Base             | 28.5                            | 15.4                           |

Data in Table 11 show that the gasoline S concentration was reduced by 26% by addition of CoAlPO<sub>x</sub>, and 13.9% by the addition of VAlPO<sub>x</sub>. The overall FCC yields (C<sub>1</sub>-

- 10 C<sub>4</sub> gas production, gasoline, LCO, and bottoms yields) changed only slightly with the CoAlPO<sub>x</sub> and VAlPO<sub>x</sub> addition, although some increases in H<sub>2</sub> and coke yields were observed. When the desulfurization results were recalculated to incorporate the gasoline-volume-loss, CoAlPO<sub>x</sub> gave 29% S reduction and VAlPO<sub>x</sub> gave 15% reduction.

5   **EXAMPLE 13 - Fluid Catalytic Cracking Evaluation of ZnAlPO<sub>x</sub>**

ZnAlPO<sub>x</sub> from Example 6 was pelleted and sized to an average particle size of approximately 70 micrometer ( $\mu$ ), then steamed in a muffle furnace at 1500°F for 4 hours to simulate catalyst deactivation in an FCC unit. Ten weight percent of steamed ZnAlPO<sub>x</sub> pellets were blended with a steam deactivated, Super Nova D<sup>TR</sup> FCC catalyst obtained  
10 from W. R. Grace. Performances of the ZnAlPO<sub>x</sub> are summarized in Table 12.

**Table 12**

|  | <i>Base Case</i> | <i>+ 10% ZnAlPO<sub>x</sub></i> |
|--|------------------|---------------------------------|
| Conversion, wt%                          | 72               | 72                              |
| Cat/Oil                                  | 3.2              | 3.6                             |
|  |                  |                                 |
| H <sub>2</sub> yield, wt%                | 0.09             | +0.03                           |
| C <sub>1</sub> + C <sub>2</sub> Gas, wt% | 1.8              | +0.2                            |
| Total C <sub>3</sub> Gas, wt%            | 5.8              | +0.3                            |
| C <sub>3</sub> = yield, wt%              | 4.9              | +0.2                            |
| Total C <sub>4</sub> Gas, wt%            | 11.3             | +0.1                            |
| C <sub>4</sub> = yield, wt%              | 5.9              | -0.2                            |
| iC <sub>4</sub> yield, wt%               | 4.5              | +0.2                            |
|  |                  |                                 |
| C <sub>5</sub> + Gasoline, wt%           | 50.0             | -1.0                            |
| LFO, wt%                                 | 23.7             | +0                              |
| HFO, wt%                                 | 4.3              | -0.2                            |
| Coke, wt%                                | 2.9              | +0.4                            |
|  |                  |                                 |
| Cut Gasoline S, PPM                      | 477              | 449                             |
| % Reduction in Cut Gasoline S            | Base             | 5.9                             |
| % Reduction in Gasoline S, Feed Basis    | Base             | 7.7                             |

5 It will be seen from Table 12 that gasoline sulfur concentration was reduced by 6% by addition of the ZnAlPO<sub>x</sub>. The overall FCC yields (H<sub>2</sub>, C<sub>1</sub>- C<sub>4</sub> gas production, gasoline, LCO, and bottoms yields) changed only slightly with the ZnAlPO<sub>x</sub> addition, although some increase in coke yield was observed. When the desulfurization results were recalculated to incorporate the gasoline-volume-loss, ZnAlPO<sub>x</sub> gave 8% S reduction.

**WHAT IS CLAIMED IS:**

1. A process for catalytic cracking of a hydrocarbon feedstock comprising contacting the feedstock with a catalyst composition comprising a mesoporous aluminophosphate material which comprises a solid aluminophosphate composition modified with at least one element selected from zirconium, cerium, lanthanum, manganese, cobalt, zinc, and vanadium, wherein the mesoporous aluminophosphate material has a specific surface of at least 100 m<sup>2</sup>/g, an average pore diameter less than or equal to 100 Å, and a pore size distribution such that at least 50% of the pores have a pore diameter less than 100 Å.
2. The process of claim 1 wherein the mesoporous aluminophosphate material has an average pore diameter of 30 to 100 Å.
3. The process of claim 1 wherein the mesoporous aluminophosphate material has a specific surface area of at least 175 m<sup>2</sup>/g.
4. The process of claim 1 wherein the mesoporous aluminophosphate material has a pore volume in the range from 0.10 cc/g to 0.75 cc/g.
5. The process of claim 1 wherein the catalyst composition further comprises a primary catalytically active cracking component.
6. The process of claim 5 wherein the weight ratio of the aluminophosphate material to the primary cracking catalyst component is about 0.01 to 0.5.
7. The process of claim 5 wherein the primary catalytically active cracking component comprises a large pore molecular sieve having a pore size greater than about 7 Angstrom.
8. The process of claim 7 wherein the primary catalytically active cracking component comprises a zeolite Y.

9. The process of claim 1 wherein the hydrocarbon feedstock contains sulfur and the process produces a gasoline boiling range product having a lower sulfur content than the feedstock.

## ABSTRACT OF THE DISCLOSURE

A process for catalytic cracking of a hydrocarbon feedstock comprises contacting the feedstock with a catalyst composition comprising a primary cracking component, such as zeolite Y, and a mesoporous aluminophosphate material which includes a solid aluminophosphate composition modified with at least one element selected from zirconium, cerium, lanthanum, manganese, cobalt, zinc, and vanadium. The mesoporous aluminophosphate material has a specific surface area of at least 100 m<sup>2</sup>/g, an average pore size less than or equal to 100 Å, and a pore size distribution such that at least 50% of the pores have a pore diameter less than 100 Å.

**Figure 1**  
**N<sub>2</sub> Pore Size Distribution**

